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### THE CURRENT STATE OF THE THEORY OF CHEMICAL STRUCTURE

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Russian Editor's Note: This is a digest of a report of the Special Commission of the Institute of Organic Chemistry, Academy of Sciences USSR, formed for the purpose of reviewing the present state of the theory of chemical structure. The report has been recommended for publication by the Scientific Council of the Institute of Organic Chemistry, Academy of Sciences of the USSR.

The Bureau  $\sqrt{ ext{Administrative Office}}$  of the Department of Chemical Sciences, Academy of Sciences USSR, has recognized the desirability of continuing the debate on the subject of structural theories which took place on 2, 3, and 7 February 1950 at an expanded meeting of the Scientific Council of the Institute of Organic Chemistry, and of transferring it to the pages of Izvestiya Akademii Nauk SSSR, Otdeleniye Khimicheskikh Nauk, Zhurnal Fizicheskoy Khimii, and Zhurnal Obshchey Khimii.

The substance of A. M. Butlerov's theory of chemical structure is the assumption that every atom in the molecule influences every other atom, either directly or indirectly. He held that when all laws which determine the dependence of the chemical properties of a substance on the structure become known, one and only one formula will express all properties of the substance. This concept differs from the ideas of Cooper and Kekule, who regarded structural formulas as reaction formulas only, drawn up mainly for purposes of convenience and easy systematization. Butlerov's theory found its classical expression in the work of V. V. Markovnikov, who asserted that the behavior of individual functional groups is not constant and invariable in all compounds, but depends on the nature of other atoms entering into the composition of the molecule, the number of these atoms, and the nature of their bonds with each other and the functional group; in short, the chemical structure of the molecule as a whole.

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Following in the steps of Butlerov, Markovnikov and many other Russian chemists made invaluable contributions to the theory of structure, which formed the foundation of organic chemical industry. The development of the industry, in turn, stimulated advances of theory. The modern theory of structure is based on experience. For that reason, it is profoundly materialistic and correctly reflects the objectively existing laws of organic chemistry, which are dialectical in nature.

Decisions of the Central Committee of the Communist Party on ideological questions and sessions of the All-Union Academy of Agricultural Sci ces imeni V. I. Lenin have mobilized all Soviet scientists for the solution o. the problem of submitting to critical analysis the contemporary state of theoretical conceptions in all fields of science and for the fight against foreign reactionary ideas of bourgeois science. The crisis of bourgeois science, which is connected with the general crisis of the capitalistic system, has also been reflected in theoretical organic chemistry as developed by bourgeois scientists, and has led to the appearance of methodologically faulty conceptions that act as a brake on scientific advances. It is typical of bourgeois scien-11515 that they underestimate Butlerov. Structural theory is interpreted in a purely formal sense which is absolutely foreign to Butlerov and his name is not even mentioned in the majority of cases. This is true of all works written by bourgeois scientists (Meyer and Jakobson, Richter-Anschuetz, Hollemann, J. Schmitt, Karrer, Fieser and Fieser), and applies particularly to treatises (including the latest books on the subject) which deal specifically with the theory of the chemical bond and chemical structure. As examples may be named Stewart's Structure of Molecules and the books by L. Pauling, G. W Wheland, and Branch.

All this constitutes falsification of historical facts in the sense that the contribution of Russian science is negated and paves the way for idealism introduced via formalistic schemes. Philosophical pragmatism is characteristic of bourgeois scientists. Thus, Paulirg defines the chemical bond and the molecule in the following manner: "We shall consider that there is a chemical bond between atoms or groups of atoms when the forces acting between them are strong enough for the formation of an aggregate which has a sufficient degree of stability to be regarded as a distinct molecule by the chemist." Any objective criterion of the reality of the molecule and the bond disappears here. It is not surprising that such premises, being methodologically, wrong, lead to absurd conclusions.

The main fault of bourgeois theoretical thinking in the field of natural science in the 20th century is "physical" idealism, particularly mathematical fetishism. As Lenin has remarked, reality disappears from the mind of reactionary theorists and is replaced by mathematical equations, so that Kant's idea to the effect that reason dictates the laws of nature is revived under a new guise. In the field of chemistry an example of this "physical" idealism is presented by the theory of resonance. In this theory, a formalistic interpretation of one of several possible methods of proximate calculation of molecules leads to the concept of an allegedly existing quantum-mechanical resonance of structures. The latter concept is then used as a means of explaining actual facts and actually existing relationships. A thorough consideration of the theory of resonance shows that there is no sound basis for introducing the concept of resonance into science: if another method of calculation is used, the concept of resonance does not arise (1).

Under the circumstances it is nonsensical to assert that resonance may determine the properties of molecules. No experimental facts confirm the existence of resonance. It has been experimentally estallished that energies are not strictly additive, but these deviations cannot be explained by a nonexistent resonance of structures.

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Pauling and his followers substitute for the actual molecule a fictitious set of resonance structures. Furthermore, Wheland expresses idealistic Machist views by stating that resonance is a purely mental concept, and then postulating the effect of resonance (i.e., of a mental concept) on the properties of molecules.

The theory of resonance has a fictitious quality of seeming to explain many facts which are not understandable to the organic chemist. For that reason, it has been widely accepted. C. K. Ingold's theory is identical with Pauling's theory, except that Ingold, in attempting to explain mesomerism and searching for some sort of special source of quantum-mechanical energy in doing so, used an energy of perturbation instead of Pauling's energy of resonance. Ingold's mesomerism is nothing else but Pauling's resonance. This also applies to the theories of Eistert (2) and Wheland, who use mesomerism in the same sense as Ingold.

It can be seen that the theoretical conceptions developed by bourgeois scientists contain a considerable element of antiscientific idealistic views. The bourgeois chemical literature is clogged with books which distort Butlerov's theory of structure and cause theoretical chemistry to advance along a wrong path.

Unfortunately, the harmful conceptions of bourgeois science have had an influence on certain Soviet scientists. Thus, Ya. K. Syrkin and M. Ye. Dyatkina state in their book, The Chemical Bond and the Structure of Molecules: "Instead of the formal structural theory of the 19th century and the primitive electrostatic ideas of the early 20th century we now have a much more highly perfected physical theory, which may serve as a point of departure for future development of the theory of chemical structure and the structure of molecules" (3). They further say: "The ideas of the formal structural theory are very simple. It is sufficient to ascribe to hydrogen one valency link represented by a dash, to oxygen two, to nitrogen three, and to carbon four, and the whole experimental material of organic chemistry will fit into this scheme." This description of the theory of structure bears no relationship to the latter's actual content. This is not surprising, because the name of Butlerov is not even mentioned a single time in the book. Distortion of the theory of structure and silent emission of the name of its creator are entirely inadmissible on the part of Soviet scientists.

Furthermore, the authors err in that they ascribe physical reality to resonance structures, although they state themselves that these structures do not actually exist. They deepen the errors of the resonance theory by computing and separating a transition structure which Pauling neglected. Their only reason for doing this is the appearance of the member  $2\frac{1}{4}$  % when the binomial ( $\frac{1}{4}$ %) is raised to the square power. Notwithstanding the fundamental errors committed by Syrkin and Dyatkina, their book was admitted as a text to be used in higher chemical educational institutions, thereby contributing to the spread of the harmful idealistic resonance theory among workers in the field of chem-

Similar errors are contained in A. I. Kipriyanov's book The Electronic Theory (4). Kipriyanov also believes in the actual existence of resonance structures. Many other examples of an uncritical attitude exhibited by Sovie's authors toward the theory of resonance can be also given. Thus, M. V. Vol'kenshteyn in his book (5) wrongly asserts that the actual state of the molecule represents a superposition of separate structures just as the state of a bond represents a superposition of elements of the homopolar and the ionic bond. S. I. Lur'ye in "Investigation in the Field of Application of the Resonance Theory to the Chemistry of Organic Compounds" (6) supplements a faulty conception of the resonance of structures, which he regards as a physical phenomenon, by entirely arbitrary discussions on the mechanism of chemical changes.

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One must note that the scientific community of the Institute of Organic Chemistry of the Academy of Sciences USSR has not paid sufficient attention to an exposition of the harmful aspects of the resonance theory. Members of this institute (including several authors of the present paper) have uncritically accepted the resonance theory and used it in their work. Examples of this use of the resonance theory are A. N. Nesmeyanov and R. Kh. Freydlina's explanation of the properties of quasi-complex compounds (7), B. M. Mikhaylov's work on organometallic compounds of anthracene (8), D. N. Kursanov's work on aromatic ethers (9), E. N. Prilezhaeva's explanation of the properties of combination dispersion spectra of ethylenic compounds (10), and lectures held by the institute's aspirant M. I. Kabachnik as well as the general review published by him.

Until recently, criticism of the theory of resonance by Soviet chemists had not uncovered the methodological faults of that theory. V. N. Ufimtsev criticizes only individual errors of the resonance theory, while G. V. Chelintsev (11) erroneously identifies the resonance theory with the whole contemporary science of chemical structure and rejects both. If localization of electrons in definite orbits is assumed, as is done by Chelintsev, a structural theory which is incompatible with the wave properties of the electron is obtained. Chelintsev's "contact" formula for benzene is incompatible with the existence of a center of symmetry in that compound and the fact that all six carbon atoms are equivalent. According to Chelintsev's theory, ethylene, butadiene, naphthalene, anthracene, and phenanthrene must have dipole moments, which is contrary to experimental facts. Chelintsev's theory contradicts the known facts of chemistry and physics to such an extent that the author does not use it himself.

Thus, Soviet organic chemists have not yet subjected to correct and sharp party criticism the idealistic conceptions of bourgeois scientists in the field of organic chemistry. The development of such criticism on the basis of Marxist-Leninist methodology and with utilization of all achievements of contemporary chemical science remains an urgent necessity.

It seems to the authors that in the future, structural theory should be developed mainly by emphasizing the mutual influence of atoms in a molecule on each other, in the sense of Markovnikov's theory. The influence of atoms on each other may be transmitted along the chains of atoms by two different means. One of them, the so-called inductior mechanism, is characteristic of 6 bonds. The influence of atoms on each other by this mechanism decreases rapidly with increasing distance. This influence is determined by the relative capacity of the electronic cloud of the 6 bond to deform, due to the action of new substituents or structural elements. Deformation also takes place due to the effect of an external field.

Another type of interaction between atoms is characterized by the mutual effect of groups possessing  $\mathcal T$  bonds, particularly conjugated bonds of this type. This is the so-called tautomeric mechanism. The electronic cloud of the bonds is much more easily deformed than that due to the 6 bonds with the result that the electronic cloud is more equally distributed along a conjugated chain and there is a higher degree of polarizability.

Both mechanisms are realized in a molecule which does not react (static effects) as well as in a molecule which is entering a chemical reaction (dynamic effects). In the latter case, the influence of other reactants will affect the distribution of the electronic cloud.

At the present stage, only a qualitative evaluation of the distribution of electronic density along a molecule is possible.

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Successes achieved in the investigation of the mutual effect of atoms on each other have led to a better understanding of the structure of substances which cannot easily be depicted by conventional structural formulas (aromatic compounds and straight chain compounds having conjugated bonds). The uniform distribution of the electronic cloud in such compounds and the equivalence of all carbon atoms in aromatic molecules lead to a structure which has been rather unfortunately described as due to a "dislocation" of bonds. The peculiarities of the chemical structure of such compounds result in a higher heat of formation than that which would be expected on the basis of simple additivity, and deviations in the values of other chemical constants are also observed.

The conception of the conjugation of simple (6) bonds among themselves and with multiple bonds is now being developed by Soviet chemists and will form the basis for a further advance of the structural theory of interatomic effects.

Although the first systematization of electronic displacements was proposed in the early 1930's by Ingold, he confused mesomerism with Pauling's resonance. It is clear from what has been said above that mesomerism, which is only one of the forms of the mutual influence of atoms in a molecule on each other (cf Ingold's systematization), cannot be regarded as due to a fictitious resonance of structures.

It seems to the authors that the tern "mesomerism" has been distorted by its use in the sense of the resonance theory to such an extent that it would be expedient to replace it with another term. Chemists usually picture the mesomeric state as an intermediate structure. When a chemist encounters characteristic chemical and physical properties which are due to the mutual influence of atoms and groups on each other, he compares the properties of the atoms and groups in question with those of the same atoms and groups in other, structurally related compounds. He then concludes that the distribution of electronic density in the compound in question is intermediate between the distribution in compounds and groups used for comparison. This is A. N. Nesmeyanov's conception of the intermediate structure (12), and it differs radically from the ideas of the intermediate state developed by F. Arndt (13), Ingold (14), Wheland (15), and others, who compare a really existing molecule with fictitious "limiting," "unperturbed," and other structures (i.e., resonance structures).

While Ingold, Robinson, and other representatives of the English school have contributed something positive to the creation of the electronic theory of reactivity of organic compounds, Ingold's theory, even when supplemented by the idea that a single bond is capable of conjugation with a double bond, is entirely inadequate, because it does not by far embrace all the possible types of mutual influence of atoms in a molecule on each other. Particularly, the whole chemistry of free radicals and all homolytic reactions (i.e., reactions which are accompanied by the splitting up of electronic pairs) are not covered by Ingold's systematization and do not fit into it.

As far as formulation is concerned, it is true that conventional formulas do not express entirely accurately the chemical structure of compounds. Certain advantages may be connected with expressing the structure by a set of several formulas, but the drawback of this method is that an erroneous idea in regard to the polystructural quality of the molecule may arise, while the molecule has only a single, very definite structure. The necessity of creating a method which expresses the mutual effects of atoms on each other in a single formula corresponding to objective reality must be emphasized.

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Application of quantum mechanics, notwithstanding the approximate character of calculations, has resulted in proof that the conception in regard to the dislocation of bonds which chemists had formed on the basis of experimental data was correct. Another positive achievement is the modern theory of the activated complex in chemical reactions (theory of the absolute velocities of reactions), the qualitative results of which have been applied in organic chemistry.

Butlerov's structural theory has advanced considerably with the aid of the latest achievements of quantum physics. Nevertheless, theoretical organic chemistry does not yet cover many known relationships and experimental facts. Contemporary electronic theory is still mainly quantitative, so that its application is restricted in cases when a qualitative relationship is of decisive importance. Many relationships which have been experimentally determined for saturated compounds cannot be explained by the theory. The theory of reactivity which is based on the subdivision of reactive substances into nucleophilic reagents, electrophilic reagents, and radicals is still inadequate in many respects. Questions connected with the structure of the activated complex (the intermediate state in chemical reactions) have only begun to be studied. The problem of the effect of reaction media on reactivity of organic compounds is still at an early stage of investigation, as far as theoretical explanation is

In the field of theoretical organic chemistry, the task of Soviet chemists will comprise further development of Butlerov's theory of structure with the aim of overcoming the defects of the contemporary electronic theory and creating a more general and qualitative electronic theory. The important problems here are a general solution of Markovnikov's problem, solution of the problem of interdependence between the chemical structure and the physical properties of organic compounds, and creation of a more perfect theory of chemical reactions of organic compounds. In the theoretical field, Soviet chemists must generalize the extensive experience of the Soviet organic chemical industry acquired in all practical applications which are dependent on organic chemistry, and achieve the broadest utilization of theoretical results in the practical tasks of building Communism in the USSR.

There is no doubt that Soviet chemists educated in the great tradition of Russian chemistry, armed with Marxist-Leninist ideology, and led by the Communist Party will successfully fulfill the tasks which lie before them.

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